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Three-Way Regeneration of Spent V_2O_5 Catalyst from Sulfuric Acid Production

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Abstract:-The general context of this work is the regeneration of the catalyst based on vanadium pent oxide. The purpose of regeneration is the reuse of the catalyst after a lifetime that does not exceed ten years. To accomplish this task, we proceeded according to three different methods of regeneration; thermal, chemical and chemical coupled with electromagnetic treatment. Catalytic tests were conducted in a micro reactor to decide on the most efficient regeneration method. The experimental results of the catalytic tests of the regenerated catalyst by the chemical and thermal method have showed a delay in triggering the conversion compared to the fresh catalyst. In order to overcome this phenomenon, we have tried the method of chemical regeneration coupled with an electromagnetic treatment given the importance of the impregnation stage in the increase of the active phase and the primordial role of the electromagnetic waves in the creation of pores and the improvement of the dispersion of the active phase. This method has recovered more than 80% of spent catalyst activity.

***Keywords**:- Vanadium pent oxide, Spent catalyst, Deactivation; Regeneration; Micro reactor; Catalytic tests.*

I. INTRODUCTION

Sulfuric acid is considered to be an economic indicator of several countries because of its wide use for the transformation of phosphate rock into phosphoric acid itself used to make phosphate fertilizers [1]. Worldwide production of sulfuric acid was estimated in 2012 at 250 million tons with an increase of 20 million tons in 2017[2].

The production of sulfuric acid is ensured by the contact process, of which the determining step is the catalytic oxidation of SO_2 to SO_3.

This oxidation reaction is exothermic and is initiated at a temperature between 410 and 440 °C in a catalytic converter. The catalyst consists of 4-9 wt% vanadium pentoxide V_2O_5, being the active component, together with alkali metals as promoters [3]. During its use, this catalyst undergoes mechanical and/or chemical alterations which cause its deactivation and subsequently the degradation of its catalytic performance. Over time, the catalyst loses its catalytic activity and / or its selectivity called deactivation of the catalyst. The deactivation of the catalyst presents a great problem in the practice of industrial catalytic processes. Typically, the loss of activity in a well-controlled process occurs slowly.

There are several mechanisms of different types that are responsible for the deactivation of catalysts as poisoning which is a chemical deactivation where chemical species modify and even suppress the properties of the catalyst by blocking its active sites. We can also mention the fouling which consists of a physical deposition of species of the fluid phase on the surface of the catalyst which causes a loss of activity due to the blocking of the sites and/or pores [3,4]. Other types of deactivation may be encountered such as thermal degradation and sintering where deactivation is both thermal and chemical. Crushing is also a source of mechanical deactivation of the catalyst due to the loss of its internal surface due to the mechanical crushing between the different particles of the catalyst [4].

The industrial experience with GCT in Tunisia (Tunisian Chemical Group) shows that the lifetime of vanadium pent oxide varies between 5 and 10 years and after this period it will be replaced by a new catalyst. Within GCT, several hundred tons of this catalyst, classified as toxic and dangerous for the environment is stored without treatment or reuse.

In order to put an end to this strong deterioration of the catalyst, which presents not only a problem for the industry but also a danger for the environment, we propose in this work to regenerate the spent catalyst by 3 ways. This regeneration is a kind of re-newly catalytic properties of the catalyst and improving its performance which allows its reuse.

Several attempts to regenerate spent catalyst have been developed by some researchers. R. Khodayari et al. and X. Xinya et al. studied acidification regeneration and recovered a portion of the catalytic activity. Other regeneration types were tested using a gas (NH_3, H_2 or Ar) ensuring the blocked pore release. Despite the paucity of bibliographic data on the regeneration of vanadium pent oxide catalyst, almost all work shows that chemical and thermal regeneration must be coupled to cope with both chemical and physical deactivation [3,4,5].

The present work aims to compare three techniques of chemical, thermal and chemical regeneration coupled with electromagnetic treatment [6, 7,8].

To validate the regeneration methods thus proposed, a catalytic activity test is carried out in a micro reactor to minimize the amount of the raw material used, namely sulfur dioxide and oxygen.

The choice of a miniaturized reactor, which is an approach, according to several research works, both effective and innovative has also made it possible to overcome the thermal and material limitations [7, 8, and 9].

II. EXPERIMENTAL PROCESSES

In this part, we present the different regeneration protocols of the spent catalyst based on vanadium pent oxide and the experimental device for carrying out the catalytic tests.

A. Regeneration Methods

Three regeneration methods were tested in this work. The thermal, chemical and chemical methods coupled with the microwave are represented in the following. Each method follows a precise procedure for treating and conditioning the spent catalyst.

➢ *Thermal regeneration*

For thermal regeneration, temperature is the main factor that manages the regeneration of the used catalyst.

This treatment is performed in an electric oven that can reach very high temperatures of the order of 1000°C. The variation of the temperature in the oven can be programmed as a function of time.

A sample of 10 g of spent catalyst is washed with water and then heated in the oven at a temperature of 500°C for one hour.

➢ *Chemical regeneration*

Chemical regeneration involves the reactivation of spent catalyst using chemicals. This method is carried out in three successive stages namely washing, acidification and drying.

Catalyst Washing: A spent catalyst sample, with a mass of 500 g, is washed five times with distilled water for 15 minutes each, under magnetic agitation.

At the beginning of the washing, a coloring of the water is observed. This coloration can be explained by the impurities emitted by the catalyst. Then, the coloration of the washing water becomes less and less intense, which confirms that any impurity that can be trapped by the washing solution has been eliminated. After the fifth wash, we noticed the disappearance of the color [8, 9,10].

Catalyst Acidification: After washing, the catalyst is placed in one liter of distilled water containing 10 ml of sulfuric acid (98%). After a few seconds, a slightly greenish color appeared. It should be noted that the coloration of the solution is accompanied by a change in the color of the catalyst from black-purple to yellow. This change can be explained by an elimination of the impurities not recovered by the washing water but also by an oxidation reaction on the catalyst surface. Indeed, the change in the color of the catalyst is according to the degree of oxidation of Vanadium. It can be seen that the black-purple color corresponds to a degree of oxidation equal to +3 while the yellow color corresponds to a +4 degree of oxidation [11].

Catalyst Drying: After the acidification step, the catalyst sample is put in an oven for two days at a temperature equal to 60 °C. The purpose of this drying step is the removal of the humidity and the desorption of the various contaminants from the catalyst. In order to improve the performance of our sample, we carried out an additional drying step that took place in the electric oven for 20 min at 200 °C.

➢ *Chemical regeneration with electromagnetic treatment*

The chemical regeneration with an electromagnetic treatment is mainly based on the use of a NH_4VO_3 which is the essential element of the impregnation stage and the use of microwave for electromagnetic treatment.

In order to carry out regeneration by microwave, we have proceeded as follows:

- Wash of 10 g of the spent catalyst with 100 ml of a mixture of distilled water and ethanol (20%) under magnetic agitation during 15 min.
- Microwave heating at 700W during 7 min.
- Impregnation of catalyst in a solution of oxalic acid (100 ml) containing NH_4VO_3 (5%), this step takes place during 2h at room temperature.
- Microwave heating at 700W for 7 min.
- Calcination at 600 °C for 1h.

B. Activity Test of catalyst

To make the catalytic test, we used a micro reactor. So our test is at the micro scale which requires a prior preparation of the catalyst. Figure 1 illustrates the experimental device used.

In order to be introduced into the micro reactor, the catalyst is crushed and sieved to obtain the desired particle size. In our experience, we used two successive screens of 500 and 200 micrometers [9].

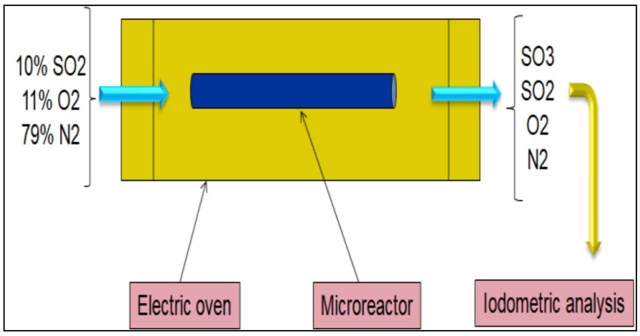

Fig1:- Experimental device.

The experimental setup consists of:

Micro reactor: tubular bed reactor packed in stainless steel. Its diameter is equal to 4 mm and its length is equal to 10 cm.

Oven: It is an electric furnace with variable temperature that can reach a temperature equal to 1000 °C. The utility of the latter is to vary the temperature until it reaches the necessary temperature range for a conversion of SO_2 into SO_3. The oven is equipped with a thermocouple installed in the catalytic bed to monitor the temperature in the micro reactor.

To develop sulfuric anhydride (SO_3), we used a sulfur dioxide (SO_2), oxygen (O_2) and of nitrogen (N_2) bottles.

The gaseous mixture feeds the micro reactor and meets the catalyst where the reaction will take place from a temperature of 420 °C At the output of the micro reactor the amount of unconverted SO_2 is estimated by the iodometric method, in order to determine the SO_2 conversion rate which gives us information on the activity and yield of the catalyst [9, 10, 11].

III. RESULTS AND DISCUSSIONS

A. Influence of the flow rate on the conversion

As a first experiment, the activity of the fresh catalyst was tested by varying in each case the total flow rate of the gas flow supplying the micro reactor, the purpose of which is to see the impact of this variation on the oxidation rate of SO_2 into SO_3.

Figure 2 summarizes the variation of conversion as a function of temperature for three different flow rates of the gas mixture.

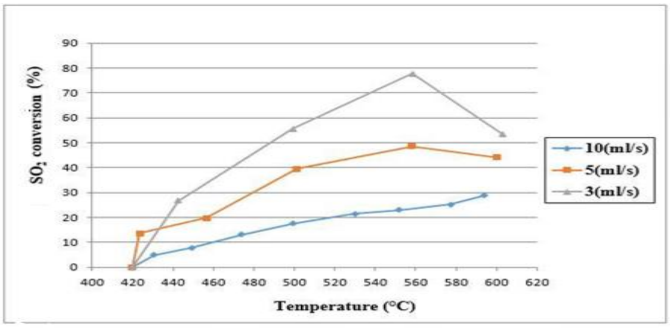

Fig 2:- Variation of conversion as a function of temperature for three different flow rates of the gas mixture.

This figure shows that the best conversion is obtained for the lowest flow (3 mL/s). Indeed, when the flow rate decreases the residence time of the reagents in the micro reactor increases which promotes the contact and the reaction between them. On the other hand, we note that the conversion rate increases gradually for the three volume flows as a function of temperature. Then the conversion rate drops from the temperature of 558°C. In fact, this variation of the conversion rate as a function of the temperature depends on the variation of the equilibrium constant Kp:

$$K_p = e^{\left[-10{,}68+\frac{11300}{T}\right]} = \frac{[SO3]}{[SO2][O2]^{0,5}}$$

This equilibrium constant versus temperature of reaction is represented by Figure 3.

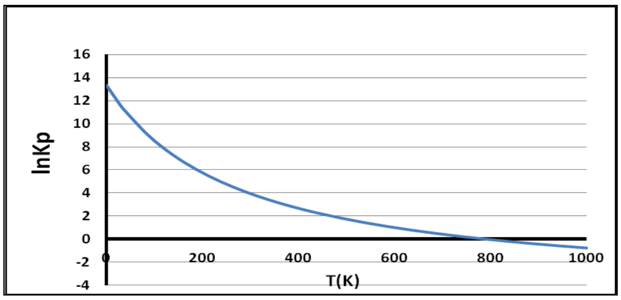

Fig 3:- Equilibrium constant versus temperature of reaction.

When Kp> 1 ie (ln (Kp)> 0) The reaction is promoted in the direct direction that is to say the direction of production of SO3 which increases the conversion rate.

When Kp <1 ie (ln (Kp) <0) The equilibrium moves in the opposite direction which leads to the decrease of the conversion rate.

B. Influence of the temperature on the conversion rate

Temperature is one of the main parameters that influence the conversion rate. To translate this influence, we plotted the curve of the variation of conversion rate as a function of the reactor temperature (Figure 4).

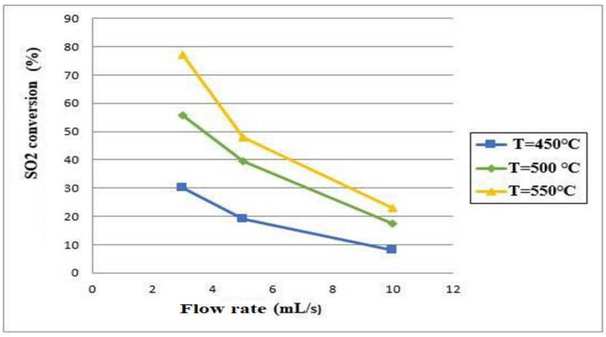

Fig 4:- Variation of conversion rate as a function of the reactor temperature.

This figure shows that the conversion rate increases, for a fixed flow, when the temperature increases. This observation is limited, as already mentioned by the equilibrium constant which in turn depends on the temperature. From a certain temperature limit, the equilibrium constant becomes less than unity and the conversion rate drops.

C. Variation of the conversion using the regenerated catalyst by a chemical method

To test the regenerated catalyst by the chemical method, we set the total gas flow rate equal to 3 mL/s to have the best possible conversion rate. In addition, we took various samples at several temperatures to follow the conversion of SO_2 to SO_3.

From Figure 5, we can see that the conversion by the regenerated catalyst did not take place until the temperature of 500 °C and the conversion rate begins to evolve until reaching a maximum of 62% at 600 °C.

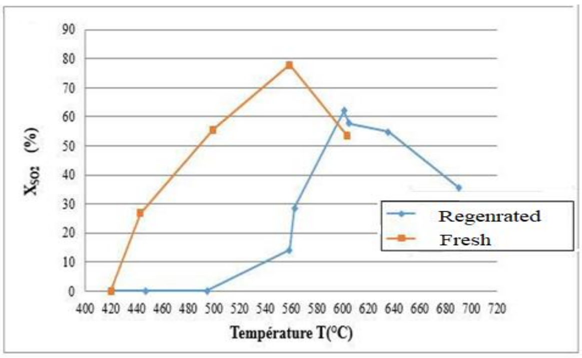

Fig 5:- Comparison of conversion versus Temperature for fresh and chemical regenerated catalyst.

The catalytic conversion for the regenerated catalyst is triggered for a temperature higher than that of the fresh catalyst. This trigger delay is certainly related to the physicochemical properties of the catalyst obtained after regeneration. A systematic interpretation of this phenomenon is based on the heat treatment time of the regenerated catalyst which appears to be insufficient. Indeed, after chemical treatment, the catalyst is heated in an oven at two different temperatures; 60°C and 200°C respectively for 2 days and 20min. This heating time has not been optimized and may be short. The missing heating time was, therefore, completed in the micro reactor, heated in turn to carry out the conversion reaction.

On the other hand and based on the work of U. Bentrupet al. and S.B Rasmussen et al. in which a characterization by ATG and ATD of spent catalysts, we can explain this shift as follows: A loss of mass of spent catalyst of the order of 19% compared to the fresh catalyst was identified from a temperature equal to 470 ° C. This decrease in mass can be attributed to the release of H_2S (sulfur hydroxide) and SO_2 from the spent catalyst at this temperature level. For our case, the offset may be due to the persistence of H_2S and SO_2 even after the heat treatment which blocks the pores of the catalyst and delays the production of sulfur trioxide. In addition, potassium is one of the main promoters of the catalyst which can react in the presence of sulfuric acid to give KHS_2O_7 (potassium hydrogen sulphate). In general, the latter melts at 200°C and changes phase. This phase change certainly requires additional heat input and delays the conversion of SO_2 to SO_3 [9,10,11].

D. Variation of the conversion using the catalyst regenerated by the thermal method

As in the previous case, the evolution of the conversion rate in the presence of the regenerated catalyst by the thermal method we set the total flow rate of gas flow at 3 mL/s and we started the heating to take samples at different temperatures.

From the figure 6, we notice that the conversion by the regenerated catalyst is triggered only at high temperatures (from 510°C). At 611.7°C the conversion rate is almost 48%.

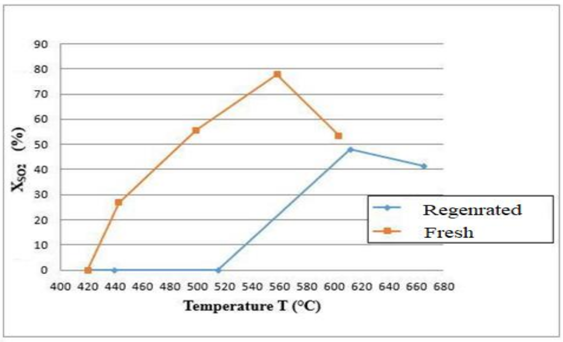

Fig 6:- Comparison of conversion versus Temperature for fresh and thermal regenerated catalyst.

This delay in triggering the conversion of the regenerated catalyst (T = 510 °C) relative to the fresh catalyst (T = 420 °C) can be explained by the change in the physicochemical properties of the catalyst after regeneration. As a first interpretation the time of heat treatment (one hour) is judged insufficient. On the other hand, as we have already mentioned, that the delay may be due to the persistence of H_2S and SO_2. From which we can confirm that the heat treatment did not release them completely, which prevents the conversion of SO_2 to SO_3 from 420 °C

E. Variation of the conversion using the catalyst regenerated by the microwave method

For the same operating conditions mentioned above, we carried out the catalytic test to convert SO_2 to SO_3 on a catalyst regenerated using a microwave oven.

From figure 7 we can see that the conversion by the regenerated catalyst is triggered from 421 ° C at the same time as the fresh catalyst with a conversion rate of about 13%. This conversion rate reaches 81% at 603.5 C.

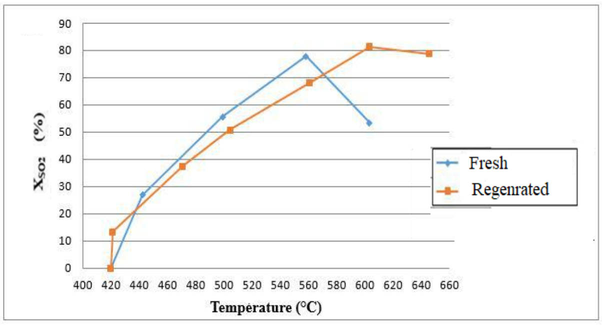

Fig 7:- Comparison of conversion versus Temperature for fresh and chemical+ microwave regenerated catalyst.

This result can be explained by the fact that the electromagnetic treatment makes it possible to get rid of any impurities leading to the blocking of the conversion.

F. Comparison of different catalyst regeneration methods

Table 1 summarizes the catalytic activity results of fresh catalyst and catalysts regenerated by the three methods.

Catalyst	Conversion (%)	Conversion trigger temperature (°C)
Fresh	78	421
Regenerated by thermal method	48	510
Regenerated by chemical method	62	500
Regenerated by the microwave method	81	421

Table 1.

The comparative study of the different methods shows that the thermal and chemical methods have made it possible to recover a part of the catalytic activity but need to be supplemented by thermal treatment to avoid the phenomenon of delayed release of the reaction.

In order to overcome this problem, the method of chemical regeneration coupled with electromagnetic treatment seems to be very effective. Indeed, considering the importance of the impregnation stage in the increase of the active phase and the primordial role of the electromagnetic waves in the creation of the pores and the improvement of the dispersion of the active phase, this method allowed the recovery of more than 80% of the catalytic activity.

IV. CONCLUSION

The context of this work is the establishment of a regeneration method of the catalyst-based vanadium pent oxide. The purpose of regeneration is the reuse of the catalyst after a lifetime that does not exceed ten years. To ensure this task, we proceeded according to three different ways namely the thermal pathway, the chemical pathway and the chemical pathway coupled with electromagnetic treatment. Catalytic tests were conducted in a micro reactor to decide on the most efficient regeneration method. The experimental results of the catalytic tests of the regenerated catalyst by the chemical and thermal method have shown a phenomenon of shift of the triggering temperature of the SO_2 conversion reaction. This shift is due to several reasons, the main ones being:

The physicochemical changes of the catalyst after regeneration which lead to insufficient time spent for the heat treatment that will take place at the level of the micro-reactor Clogging of the catalyst pores with H_2S and SO_2 which do not completely liberate during the heat treatment and therefore delays the progress of the conversion reaction.

The addition of sulfuric acid and the reaction of the latter with potassium to give KHS_2O_7. This compound changes phase to 200°C which certainly requires additional heat input and delays the conversion of SO_2 to SO_3.

In order to overcome the shift phenomenon, we have tried the method of chemical regeneration coupled with an electromagnetic treatment given the importance of the impregnation stage in the increase of the active phase and the primordial role of the electromagnetic waves in the creation of pores and the improvement of the dispersion of the active phase. This method allowed the spent catalyst to recover more than 80% of its initial activity. This study must be continued by the characterization of fresh, spent and regenerated catalysts in order to better explain the SO_2 conversion in each case of regeneration prior to optimize the operating conditions.

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